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Description

Thermoplastic mixtures for implanting electrical modules in a card body

The invention relates to thermoplastic mixtures, which are activated with an implanting die at 150°C and are used for bonding electrical modules to card bodies.

In relation to the implanting of electrical modules in card bodies the prior art has already disclosed a multiplicity of adhesive sheets or joining methods. The aim of such implantations is to produce telephone cards, credit cards, parking machine cards, insurance cards, etc. Examples of the corresponding adhesive bonding methods are found for example in patents EP 0 842 995 A, EP 1 078 965 A, and DE 199 48 560 A.

In this field of adhesive bonding, however, the bar is continuously being raised as regards the requirements imposed on the adhesive system. For instance, the adhesive must adhere well to polycarbonate, to ABS, PVC, and PET, and also to the electrical module. Bonding here is generally to epoxy materials, polyesters or polyimides. At one time cyano acrylates were used as liquid adhesives, and have the advantage of optimum wetting of both the card body and the electrical chip. This technology, however, is dying out, since the operations are very slow. The evaporation of the solvent from the cavity in the card body was slow; the metering nozzles became blocked during downtime, as a result of drying out, and were also of poor meterability; and the liquid adhesive likewise required a certain time for curing. As a result, the quality of adhesive bonding was decidedly poor.

It is here that the hot-melt adhesives prove markedly superior to their liquid counterparts. Nevertheless, here as well, the selection of suitable compounds is very limited, owing to the exacting requirements imposed on this joining technique. One restriction involves the very different materials that must be bonded. Owing to the very different polarities of PC, PVC, PET, ABS, epoxy, and polyimide, it is impossible to find a single polymer which

adheres equally well to all materials. One possibility of raising the adhesion on various substrates is to mix different adhesives. Here as well, however, the problem exists of obtaining a stable mixture which does not undergo phase separation after a number of weeks, thereby in turn impairing the adhesion. This is particularly so even for relatively long storages at elevated temperatures.

Moreover, the requirements imposed by the end customers are rising further and further. For example, the flatness of the electrical module with the card body is an important criterion, since otherwise it would no longer be possible to read the cards. This implies an upper limit on the implanting temperatures, since, for example, PVC in particular tends to deform at implanting temperatures above 170°C.

Another criterion is the requirement from the banking sector that the electrical modules should not be able to be removed without destruction. Accordingly the internal cohesion of the adhesive must be very high, so that it does not split in the middle and the adhesion to either side (card body + electrical module) is extremely high. At the same time, however, the adhesive must also have a very high flexibility, since following implantation the cards pass through torsion tests and a flexural test. Preferably the card material ought to break before any failure of adhesion to the card body and to the electrical module. In general not even instances of lifting at the edge are tolerated.

A further criterion are temperature fluctuations and the effect of moisture, since in the course of their subsequent use these cards must withstand both high and low temperatures and in some cases are even required to survive a transit through the wash. Accordingly, the adhesive ought not to become brittle at low temperatures, ought not to liquefy at high temperatures, and ought to possess a low propensity to absorb water.

A further requirement criterion, owing to the growing numbers of card demand, is the processing speed. The adhesive ought to soften or melt very quickly, so that the implanting operation can be concluded within a second.

The object on which the invention is based, in view of this prior art, is that of specifying an adhesive sheet for implanting electrical modules in a card body, the said sheet meeting the criteria specified above and developing very high adhesion to the different card bodies and electrical modules in the die in particular at implanting temperatures of 150°C.

In accordance with the invention the object is achieved by means of an adhesive sheet composed of a mixture of thermoplastics T1 and T2, wherein the adhesive system

a) has a softening temperature of greater than 65°C and less than 125°C,
b) a storage modulus G' at 23°C, as measured by test method A, of greater than 10^7 Pas,
c) a loss modulus G" at 23°C, as measured by test method A, of greater than 10^6 Pas,
d) and a crossover, as measured by test method A, of less than 125°C.

The crossover temperature must be below 125°C, since otherwise the adhesive will not become fluid and hence would not provide optimum wetting either of the card surface or of the electrical module. At the crossover point there is intersection of the storage modulus G' and loss modulus G" curves; physically this can be interpreted as the transition from elastic to viscous behavior.

Furthermore, the elastic component, i.e., the storage modulus G', must be greater than 10^7 Pas, and the viscous component, i.e., the loss modulus G", must be greater than 10^6 Pas, since otherwise the adhesive is not ensured optimum flexibility. The adhesive must ensure the loadings that occur between card body and electrical module even under instances of severe distortion. Hence the need for a rheologically optimized viscoelastic behavior.

As a result of the inventive mixing of the thermoplastic blends an improvement in the adhesion to the card body is achieved which cannot be achieved with the singular thermoplastics.

The adhesive bonding of the electrical module 2 to a card body 3 is depicted diagrammatically in Fig 1. The inventive temperature-activable adhesive 1 possesses a layer thickness of between 10 and 100 µm in one preferred version and a layer thickness of 30 to 80 µm in a particularly preferred version.

Heat-activable thermoplastic mixtures

The heat-activable adhesive is composed of a blend of at least two thermoplastic materials T1 and T2.

In one preferred version two different thermoplastic polymers are mixed with one another. The mixing ratio of the two thermoplastics T1 and T2 is between 5:95 (T1:T2) and 95:5 (T1:T2). In one preferred version the mixing ratio is between 10:90 (T1:T2) and 90:10 (T1:T2).

In one very preferred version the thermoplastic materials T1 and T2 are selected independently of one another from the group of the following polymers: polyurethanes, polyesters, polyamides, ethylene-vinyl acetates, synthetic rubbers, such as styrene-isoprene diblock and triblock copolymers (SIS), styrene-butadiene diblock and triblock copolymers (SBS), styrene-ethylene-butadiene diblock and triblock copolymer (SEBS), polyvinyl acetate, polyimides, polyethers, copolyamides, copolyesters, polyolefins, such as polyethylene, polypropylene, or poly(meth)acrylates, for example.
The enumeration makes no claim to completeness.

In a further embodiment of the invention thermoplastic blends are selected from one polymer group, the polymers then differing in their chemical composition.

In order to achieve the activation temperature of below 125°C at least T1 or T2 ought to possess an activation temperature below 125°C.

The thermoplastic blend possesses a softening range of between 65 and 125°C.

In addition at least one of the thermoplastics, T1 or T2, possesses

a) a storage modulus G' at 23°C, as measured by test method A, of greater than 10^7 Pas,

b) a loss modulus G" at 23°C, as measured by test method A, of greater than 10^6 Pas,

c) and a crossover, as measured by test method A, of less than 125°C.

To optimize the technical adhesive properties and the activation range it is possible to optionally add bond strength-enhancing resins or reactive resins. The proportion of the resins is between 2% and 50% by weight based on the thermoplastic mixture.

Tackifying resins for addition that can be used include, without exception, all tackifier resins that are already known and described in the literature. Representatives that may be mentioned include the pinene resins, indene resins, and rosins, their disproportionated, hydrogenated, polymerized, and esterified derivates and salts, the aliphatic and aromatic hydrocarbon resins, terpene resins, and terpenephenolic resins, and also C5, C9, and other hydrocarbon resins. Any desired combinations of these and further resins may be used in order to adjust the properties of the resultant adhesive in

accordance with requirements. Generally speaking it is possible to use all resins that are compatible with (soluble in) the thermoplastic; reference may be made in particular to all aliphatic, aromatic, and alkylaromatic hydrocarbon resins, hydrocarbon resins based on single monomers, hydrogenated hydrocarbon resins, functional hydrocarbon resins, and natural resins. Express attention is drawn to the depiction of the state of knowledge in the "Handbook of Pressure Sensitive Adhesive Technology" by Donatas Satas (van Nostrand, 1989).

In a further embodiment, reactive resins are added to the thermoplastic mixture.

One very preferred group embraces epoxy resins. The molecular weight M_W (weight average) of the epoxy resins varies from 100 g/mol up to a maximum of 10 000 g/mol for polymeric epoxy resins.

The epoxy resins embrace, for example, the reaction product of bisphenol A and epichlorohydrin, the reaction product of phenol and formaldehyde (novolak resins) and epichlorohydrin, glycidyl esters, the reaction product of epichlorohydrin and p-aminophenol.

Preferred commercial examples are Araldite™ 6010, CY-281™, ECN™ 1273, ECN™ 1280, MY 720, RD-2 from Ciba Geigy, DER™ 331, DER™ 732, DER™ 736, DEN™ 432, DEN™ 438, DEN™ 485 from Dow Chemical, Epon™ 812, 825, 826, 828, 830, 834, 836, 871, 872,1001, 1004, 1031 etc. from Shell Chemical, and HPT™ 1071, HPT™ 1079 likewise from Shell Chemical.

Examples of commercial aliphatic epoxy resins are vinylcyclohexane dioxides, such as ERL-4206, ERL-4221, ERL 4201, ERL-4289 or ERL-0400 from Union Carbide Corp.

Examples of novolak resins which can be used include Epi-Rez™ 5132 from Celanese, ESCN-001 from Sumitomo Chemical, CY-281 from Ciba Geigy, DEN™ 431, DEN™ 438, Quatrex 5010 from Dow Chemical, RE 305S from Nippon Kayaku, Epiclon™ N673 from DaiNipon Ink Chemistry or Epicote™ 152 from Shell Chemical.

As reactive resins it is possible in addition to use melamine resins, such as Cymel™ 327 and 323 from Cytec.

As reactive resins it is also possible, furthermore, to use terpene-phenolic resins, such as NIREZ™ 2019 from Arizona Chemical.

As reactive resins it is also possible, furthermore, to use phenolic resins, such as YP 50 from Toto Kasei, PKHC from Union Carbide Corp., and BKR 2620 from Showa Union Gosei Corp.

As reactive resins it is also possible, furthermore, to use polyisocyanates, such as Coronate™ L from Nippon Polyurethan Ind. and Desmodur™ N3300 or Mondur™ 489 from Bayer.

In order to accelerate reaction between two components it is also possible, optionally, to additize crosslinkers and accelerants into the mixture.

Examples of suitable accelerants include imidazoles, available commercially as 2M7, 2E4MN, 2PZ-CN, 2PZ-CNS, P0505, L07N from Shikoku Chem. Corp. or Curezol 2MZ from Air Products.

In addition it is also possible to use amines, especially tertiary amines, for acceleration.

Besides reactive resins it is also possible to employ plasticizers. Here, in one preferred embodiment of the invention, plasticizers based on polyglycol ethers, polyethylene oxides, and phosphate esters can be used, as can aliphatic carboxylic esters and benzoic esters. In addition it is also possible to use aromatic carboxylic esters, diols of relatively high molecular mass, sulfonamides, and adipic esters.

A further possibility is to add optionally fillers (e.g., fibers, carbon black, zinc oxide, titanium dioxide, chalk, solid or hollow glass spheres, microspheres made of other materials, silica, silicates), nucleators, expandants, compounding agents and/or aging inhibitors, in the form for example of primary and secondary antioxidants or of light stabilizers.

In a further preferred embodiment of the pressure-sensitive adhesive tape of the invention use is made for the thermoplastics T1 or T2 of polyolefins, especially poly-α-olefins, where at least one thermoplastic T1 or T2 has a softening temperature of greater

than 65°C and less than 125°C and likewise resolidify after adhesive bonding, in the course of cooling. The company Degussa makes a number of different heat-activable poly-α-olefins available commercially under the trade name Vestoplast™.

In one preferred embodiment the thermoplastic mixtures have static softening temperatures $T_{s,a}$ or melting points $T_{m,a}$ of 65°C to 125°C. The bond strength of these polymers can be raised by means of controlled additization. Thus it is possible, for example, to use polyimine copolymers or polyvinyl acetate copolymers as bond strength promoter additives.

The heat-activable adhesive serves in particular as an adhesive sheet for bonding electrical chip modules in card bodies, the respective adhesive layer developing very good adhesion to the card body and to the electrical chip module following temperature activation.

Production process

The thermolastic blends can be produced from solution or in the melt. For producing the blend in solution it is preferred to use solvents in which at least one of the thermoplastics, T1 or T2, exhibits good solubility. The mixture is produced using the known stirring equipment. Introduction of heat may also be necessary for this purpose. Subsequently the blends are coated from solution or, more preferably, from the melt. For coating from the melt the solvent is removed from the thermoplastic blend beforehand. In one preferred embodiment the solvent is stripped off in a concentrating extruder under reduced pressure, something which can be accomplished using, for example, single-screw or twin-screw extruders, which preferably distill off the solvent in different or identical vacuum stages and possess a feed preheater. Coating then takes place via a melt die or an extrusion die, with the film of adhesive being drawn if desired in order to achieve the optimum coating thickness.

In a further embodiment of the invention the thermoplastic blend is produced in the melt. Blending of the resins can be carried out using a compounder or a twin-screw extruder or a planetary roller extruder.

Coating then takes place, again, from the melt. Coating takes place via a melt die or an extrusion die, with the film of adhesive being drawn if desired in order to achieve the optimum coating thickness.

Backing materials used for the thermoplastic mixture are the customary materials familiar to the skilled worker, such as films (polyesters, PET, PE, PP, BOPP, PVC, polyimide), nonwovens, foams, woven fabrics, and woven films, and also release paper (glassine, HDPE, LDPE). The backing materials ought to have been provided with a release layer. In one very preferred version of the invention the release layer is composed of a silicone release varnish or of a fluorinated release varnish.

Examples

Test methods:

Rheology A)

The measurement was carried out using a rheometer from Rheometrics Dynamic Systems (RDA II).

The Rheomatics Dynamical Analyser (RDA II) measures the torque which occurs when an oscillating shear is applied to a stripped sample (deformation control). The sample diameter was 8 mm, the sample thickness between 1 and 2 mm. Measurement was carried out using the plate-on-plate configuration (parallel plates). The temperature sweep was recorded from 0 to 150°C with a frequency of 10 rad/s.

Iso-bending B)

The Iso-bending test is carried out in analogy to the Iso/IEC standard 10373:1993 (E) – section 6.1. The test is passed if a total of more than 4000 bends is attained.

Extreme flexural test C)

In the extreme flexural test a cutout 3 cm wide, with the electrical module lying in the center, is cut from the chip card and then pressed together 10 x from a width of 3 cm to a width of 2.5 cm. The test is passed is the electrical module does not become detached.

Hand test D)

In the hand test the chip card is bent by hand over one of the two corners lying closer to the electrical module, to an extent such that the card breaks or the module breaks. The test in that case is passed. If the electrical module becomes detached or springs out, the test is failed.

Other test methods

The softening temperatures are determined preferably by way of differential scanning calorimetry (DSC).

Molar masses were determined by GPC (gel permeation chromatography) measurements. (Preparation of a solution of the sample in tetrahydrofuran with a concentration of 3 g/l; dissolution at room temperature for 12 hours; subsequently, filtration of the solution through a 1 µm disposable filter, addition of approximately 200 ppm of toluene as internal standard.

Using an autosampler, 20 µl of the solution are chromatographed as follows: a $10^{3}\oplus$ column 50 mm long is followed by one $10^{6}\oplus$, one $10^{4}\oplus$,and one $10^{3}\oplus$ column, each with a length of 300 mm. The eluent used is tetrahydrofuran, which is pumped at a flow rate of 1.0 ml/min. The columns are calibrated with polystyrene standards, detection taking place by the measurement of the change in refractive index with the aid of a Shodex differential refractometer RI 71).

Investigations

Reference 1)
Polyamide film XAF 34.408 from Collano-Xiro

Reference 2)
PU film XAF 36.304 from Collano Xiro

Reference 3)
Copolymer Grilltex 1519 from EMS-Grilltex

Reference 4)
Copolyamide Grilltex 1500 from EMS-Grilltex

Example 1)

30% by weight of Griltex 1616 E (copolyester) from EMS-Griltech and 70% by weight of Platamid 2395 (copolyamide) from Atofina were blended in a recording compounder from Haake at approximately 130°C for 15 minutes at 25 rpm. The heat-activable adhesive was subsequently extruded at 140°C between two plies of siliconized glassine release paper to 60 µm.

Example 2)

50% by weight of Griltex 1365 E (copolyester) from EMS-Griltech and 50% by weight of Griltex 1442 (copolyester) from EMS-Griltech were blended in a recording compounder from Haake at approximately 130°C for 15 minutes at 25 rpm. The heat-activable adhesive was subsequently extruded at 140°C between two plies of siliconized glassine release paper to 60 µm.

Example 3)

80% by weight of Griltex 9 E (copolyester) from EMS-Grilltech and 20% by weight of Irostic 8304 HV (thermoplastic polyurethane) from Huntsman were blended in a recording compounder from Haake at approximately 130°C for 15 minutes at 25 rpm. The heat-activable adhesive was subsequently extruded at 140°C between two plies of siliconized glassine release paper to 60 µm.

Implantation of electrical modules

The electrical modules were implanted in the card body using an implanter from Ruhlamat.

The materials employed were as follows:

Electrical modules: Nedcard Dummy N4C-25C, Tape-Type: 0232-10

PVC card: CCD

ABS card: ORGA

In a first step examples 1 to 3 are laminated at 2 bar onto the module belt from Nedcard, using a two-roll laminator from Storck GmbH.

The electrical modules are then implanted in the appropriate cavity in the card body. The parameters employed were as follows for all the examples:

Heating step: 1

Die temperature: 150°C

Time: 1 x 2 s

Cooling step: 1 x 800 ms, 25°C

Pressure: 70 N per module

Results:

The chip cards produced using the inventive adhesives were tested by methods B, C, and D. The results are set out in Table 1.

Examples	Test method B	Test method C	Test method D
1	passed	passed	passed
2	passed	passed	passed
3	passed	passed	passed

From table 1 it is apparent that all of the inventive examples met the principal criteria for a chip card and hence are very suitable for adhesively bonding electrical modules to card bodies.

Tab. 2

Reference	Test method B	Test method C	Test method D
1	passed/failed on ABS	passed/failed on ABS	failed
2	failed	failed	failed
3	passed/failed on ABS	passed/failed on ABS	failed
4	failed	failed	failed

The reference specimens in Table 2, in contrast, are significantly poorer and in particular on ABS card materials do not pass the test methods.
The rheological properties are listed in table 3 below.

Tab. 3

Examples	G' in [Pa] at 23°C	G" in [Pa] at 23°C	Crossover
1	2×10^8	4.0×10^7	113 °C
2	2×10^8	3×10^7	120 °C
3	1×10^8	4.5×10^7	120 °C